

STM CHARACTERIZATION OF COAL STRUCTURES, DERIVED EXTRACTS, MODEL  
COMPOUNDS, AND GASIFIED CARBONS:

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ABSTRACT

Techniques for characterizing coal and coal derived structures using scanning tunneling microscopy are being developed. These techniques allow surface structures of coal to be viewed with a fraction of an angstrom resolution. Images of inertinite structures have been obtained. A monolayer of THF extract from an Illinois #6 coal was deposited on HOPG and images obtained. One of the difficulties in interpreting the images is lack of knowledge about the tunneling efficiencies of various functional groups. Model compounds are being deposited onto well oriented surfaces and images at different bias and gain settings are being obtain to determine if spectral analysis can spot oxygen, sulfur, and nitrogen atoms in their various chemical forms thought to be present in coal. Analysis of pits formed from the gasification of HOPG have shown that oxygen complexes can be identified, pitting mechanisms can be followed and initial direction of gasification can be deduced. There is some evidence that oxygen complexes can form between carbon atoms of two different planes.

INTRODUCTION

The scanning tunneling microscope (STM) was invented in 1982 by Binnig and Rohrer(1), who were awarded the Nobel Prize in physics for their work. The STM operates on the principle that a tunneling current can be established between an anatomically sharp tip and the surface electronic orbitals near the Fermi level of a sample(2). An image is obtained by scanning the tip across a samples surface with the use of a set of three piezo electric crystals(3). A voltage is applied to the crystal controlling the z-direction (the distance between the tip and the sample surface). The tip is then lowered until the tip crashes into the surface(non-conducting material) or a tunneling current is established(conducting material). Once the current is established, work functions can be measured over a certain spot or xyz images can be obtained. The images are obtained by one of two operating modes. In the constant current mode varying voltages are applied to the x and y crystals which drives the tip first across the surface in the x-direction and then increments the y-spacing and drives the tip in the reverse x-direction. A feedback loop measures current and adjusts the voltage on the z-direction crystal. This raises and lowers the tip. Since current is highly dependent on distance from the surface, the variation in z-distance allows a constant current to be maintained. A computer keeps

track of the z variations in a xy matrix which is transformed by using Fourier analysis into a three dimensional image. A second mode of operations employs a constant z-setting and as the tip moves variations in current are recorded. The current xy matrix is then converted to an image.

The actual image obtained is a charge density map of the eigen states localized above a surface(4). This means that the images should be viewed in terms of electronic interactions(5,6). Interpretation of the images is therefore dependent on complex theories. Although this should be kept in mind, the images can be viewed as simple atomic geometries (5,6). For well ordered systems including silicon, gold, platinum and highly ordered graphite(7,8,9, and 10) the atomic spacings and orbital shapes agree with X-ray, and TEM data, and HMO theory.

STM is dependent on the conductivity of the sample being image. However if a sample is non-conducting then atomic force microscopy (AFM) can be used (11-15). AFM is a closely related offshoot of STM. It drags a diamond tip across the sample surface and measures the repulsion of the tip from the samples surface. the tip is set on a cantilever and a laser beam is used to measure the deflection of the cantilever. This technique is not as highly developed as STM imaging but has been used to investigate structures of polymers and ceramics.

Depending on scan size of the STM image; resolution as low as 0.01 nanometers for lateral and 0.001 nm for vertical measurements can be obtained. Scan sized can be varied from 14x14 microns to 2x2 nanometers. The depth of resolution is much greater than for SEM and TEM. In addition little or no sample preparation is required and the instrument can be operated under ambient environments with little sample preparation. Thus, surfaces can be examined in far greater detail than previously and with much less degradation of the sample. These capabilities make STM an ideal candidate for application to in situ coal structure determinations and the study of coal reactions in various conversion technologies.

The purpose of this paper is to describe some preliminary work on applying STM to coal analysis and utilization technology. To the authors knowledge this is the first work to obtain actual images of coal and coal derived materials. The paper also discusses methods used to follow gasification of highly oriented pyrolytic graphite(HOPG).

#### EXPERIMENTAL

All STM nanographs were obtained using a nanoscope II scanning tunneling microscope manufactured by Digital Instruments of Santa Barbara Ca. Details of the operating procedures can be found in reference (16). The HOPG was obtained from Union Carbide. An Illinois #6, IBCSP 101, coal was used to obtain extract and Maceral concentrates. Maceral concentrates were obtain employing a density gradient centrifugation procedures described elsewhere(17,18). THF extraction was carried out in a soxhlet extractor for 48 hours. About 20 grams of coal are extracted with 150 mls of THF. The average yield is 16% solubles based on weight of dry solids recovered after extraction.

## STM ANALYSIS OF COAL

The first attempt to image coal was made by polishing a block of coal, painting the back of the block with a conducting paint, and mounting the block on the STM base. Blocks were mounted with the tip perpendicular and parallel to the bedding plane. The instruments allows various gains and bias to be set along with scan rate and size. The tip crashed into the surface whenever engagement was attempted.

During engagement the tip is lowered manually to within 250 microns of the surface using a set of position bolts which are turned to raise or lower three ball bearings on which the STM scan head sets. The software package is then activated and automatically lowers the tip to the surface. As the tip approaches the surface it will begin to tunnel if the sample is conducting but the program will continue to lower the tip into the sample if a tunneling current is not established. Since the tip must be atomically sharp, lowering the tip to far will blunt the tip and good images will not be obtain with that tip. Since tips are expensive, this approach was abandoned after 20 attempts.

Next, particles of whole coal were scattered on the STM base. The coal was ground in an fluid energy mill prior to mounting. The smaller particles of coal were expected to be more conductive. A scan of the base was made to determine its structure before attempting to analyze the coal particles. During engagement the tip would either push particles aside and engage the base, or pin a particle and bend the tip.

Steel slides were then prepared, painted with conducting paint and coal dust was sprayed over the wet surface. This method produced a sample which could be imaged. Blank painted slides were also imaged. Although there are some differences between the blank slides and the images obtained with whole coal particles, it is difficult to describe these. (slides will be shown at the presentation). The percentage of successful engagements range between 50 and 70%. To obtain a clearer understanding of what was imaged, the process was repeated on sporinite, cutinite, vitrinite, inertinite, and mineral concentrates. The liptinites and mineral fractions could not be engaged. The Vitrinite concentrates had a 40% engagement rate and the inertinite had a 90% engagement rate. This follows the general order of conductivity of the macerals. Since most of the mineral in this coal was clay this fraction was also expected to be nonconductive.

Because of the problem with imaging the painted surfaces as well as coal particles, another approach was attempted. Coal macerals were physically pressed into a wafer with the aid of a hydraulic press. The back of the wafer was painted and the sample was mounted. Engagement was obtained for the inertinite wafer only. The images obtained with the inertinite wafer were identical to those obtained from the painted slide method. Not much can be said about the chemical structures imaged at this point. This is because there is little known about tunneling of organic structures. A good deal of model compound work will need to be carried out. It can be said that the imaged orbitals vary a great deal but the significance of these variations can not be estimated at this time. More can be said about the size and shape of the pore openings. When scanned on the nanometer range; pore diameter ranges between 5 to 20 angstroms. About half of the pores

have circular openings and half slit shape openings. Area of the slit shaped openings were greater than those of the circular openings.

#### SOLVENT DEPOSITION

Those carbon materials which are unsuitable for STM studies due to their poor conductivity, porosity, and surface heterogeneity may be imaged, in some cases, by depositing a dissolved portion (from solution) onto HOPG in very small amounts. The tetrahydrofuran (THF) soluble portion of Herrin, IL No.6 coal, as well as materials such as n-dotriacontane ( $n-C_{25}$ ), which readily dissolve in heptane, were analyzed. These solvents (THF and heptane) do not alter the HOPG surface. Blank experiments were carried out by pipeting drops of solvent on newly cleaved HOPG surfaces. After the solvent evaporates the hexagonal basal plane image of the HOPG is observed. This is somewhat unexpected because even the purest solvent contain some residual material. A quick calculation shows that the concentration is high enough to more than cover the HOPG surface. However, their usage did not effect STM images. Upon evaporation solvent/solute mixtures left behind deposited material that could be imaged.

The THF extract was diluted from its original concentration of about 0.02 gram/ml by an approximate ratio of 10:1. A portion of this solution was further diluted to approximately 100,000:1 in increments of 10:1, until STM images showed only a thin layer deposited onto the HOPG. Deposition was carried out using a pipette to place a drop of the diluted solution onto the HOPG. The THF was allowed to evaporate, leaving behind a thin layer of coal extract. The specimen could then be placed directly onto the sample stage for STM imaging. This technique is suitable for molecules with large atomic weights which adsorb strongly to the graphite surface.

Although areas could be imaged where more than a single monolayer are present these images where chaotic and individual structures were not easily recognized. A monolayer of the deposited material (or scattered areas of monolayer) gave very clear images. Various aromatic compounds are evident, as well as side-chains branching off from these rings. The images are easily differentiated from the defined HOPG basal plane surface. HOPG is an ideal substrate for organic molecules which align with the basal plane and adsorb fairly strongly, depending on the size and planarity of the molecule.

The n-dotriacontane/heptane solution was created by dissolving n-dotriacontane in heptane. This solution was deposited onto the HOPG with a micropipette. The sample was then placed directly onto the sample stage for STM imaging.

The  $n-C_{25}$  on the surface of the HOPG gave spacings of 0.30 nm, instead of 0.25 nm, between hexagon centers of the HOPG. An elliptical shape of many of the atoms was due to the hydrogen atoms attached to the carbon atoms, and the carbon atoms themselves are imaged as one. A somewhat repeating pattern on the surface was observed and believed to be due to the fact that the  $n-C_{25}$  molecules align themselves along the carbon atoms of the top basal plane layer. Other compounds such as steroids, acids, alcohols have

been imaged by others using a similar technique(19). Other model compounds such as dibenzothiophene,, thiols, carbazol and others scheduled for analysis in the near future.

#### GASIFICATION OF HOPG

In this portion of the program HOPG was exposed to air oxidation at 650°C in a TGA system until 5 and 30% burnoff was reached. After various exposure times the size, shape, and distribution of pits and the linear dimension of the graphite were determined. The STM was used to image the pits, determine the direction of oxygen attack and to determine the amount and type of oxygen complexes on the surfaces of the graphite. In the initial stage of pit formation at 5% burnoff, the pits seem to align in a parallel orientation. Also some pits extend 3-5 layers deep without enlarging. The familiar large hexagonal pits are formed by the 30% weight loss level. A zoom into the base of the pits formed at 30% weight loss showed that although the large scale hexagonal morphology is observed; attack on pristine planes is linear. Long parallel high points were observed at the end of narrow elongated pits. These high points or streaks were originally thought to be carbon atoms but cross-sectional analysis showed them to have bond lengths indicative of adsorbed oxygen molecules. The length of the streaks are multiples of 4.2 angstroms which indicate attack parallel to the 101 face. We are not sure if this is indicative of catalytic attack or if the highly oriented graphite contains a large amount of elongated crystalites. It is possible to measure bond length and depth of penetration using the cross sectional analysis routines which were provided with the STM. By measuring heights from the base of pits it is possible to obtain an idea of the composition of the atoms in the pit. For example, if the vertical distance is 3.35 angstroms then the pit is one layer deep assuming that the atoms at the pit base are carbon. Likewise an atom appearing 6.7 angstroms above the pit floor would be a carbon atom 2 layers above the floor of the pit. It is interesting to note that 3.53 and 3.22 angstroms are encountered in measurements more often than 3.35(the ideal basal plane spacing) These measurements are probably the results of edge carbon atoms wagging up or down around the pit edge. This is reasonable. In fact, edge sites on a graphite model behave the same way. Also values between these measurements are not encountered very often. Thus, any multiple of 0f 3.35 plus or minus the wag distance of 0.12 angstroms is likely to be carbon. Alternately measurements of 3.35 multiples plus or minus 0.75 and 1.5 are observed. these appear to be oxygen complexes. These values appear over and over again. The large pits have nearly vertical walls (slope > 75°) these walls are over 500 layers deep. Cross sectional analysis of smaller pits vary in angle depending on size. Some are steep like the larger pits but some have gentle slopes which seem to indicate that oxygen forms adsorbed species between layers. A similar effect was observed on edge cite studies(20,).

#### CONCLUSIONS

STM has been shown to be a powerful tool for exploring atomic structures of coal and graphite. Additional work is required to assign structures, but the techniques developed in this study demonstrate that it is possible to image coal and coal derived material.

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